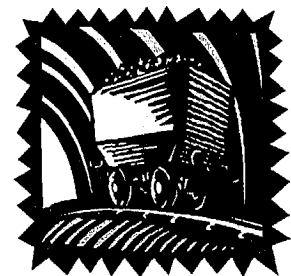


9. TRACE METALS

9. TRACE METALS	9-1
9.1 SUMMARY	9-1
9.2 PROBLEM STATEMENT	9-1
9.3 OBJECTIVE	9-1
9.4 PROBLEM DESCRIPTION	9-2
9.4.1 Water Concentrations	9-2
9.4.2 Biological Effects	9-5
9.5 APPROACH TO SOLUTION	9-6
9.5.1 Priority Actions	9-6
9.5.2 Information Needed	9-7
9.5.3 Existing Activities	9-7



9. TRACE METALS

9.1 SUMMARY

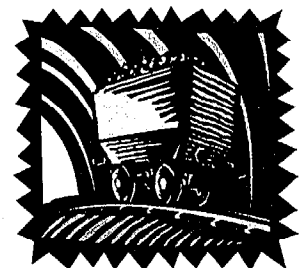
Heavy-metal loading in the watershed has been suspected as a possible source of aquatic toxicity throughout the Bay-Delta and its tributaries. Studies of abandoned mines in the upper watershed have shown toxic effects on aquatic species. Other sources in the tributaries and Bay-Delta contribute to total metal loading in the Bay-Delta. Loading in lower tributaries and the Bay-Delta causes excursions of guidelines for protection of fresh-water and marine species. Insufficient information is available to determine the ecological impacts or spatial and temporal extent of the metals in the Bay-Delta. Corrective measures should be taken in the upper watershed to protect specific species habitat. Corrective measures downstream should be based on the extent of impacts as determined by further studies.

9.2 PROBLEM STATEMENT

Heavy-metal aquatic toxicity has been documented in the upper watershed. Much of the increase in heavy-metal loading is attributed to abandoned mines. Copper loading from other sources, such as agriculture and urban discharges, adds to the total copper load to the Bay-Delta. The types and extent of ecological effects in the Bay-Delta from metal loading are not well defined.

9.3 OBJECTIVE

The objective is to reduce metal loading of the Bay-Delta and its tributaries to levels that do not adversely affect aquatic habitat, other beneficial uses of Bay-Delta estuary waters, and species dependent on the estuary.



9.4 PROBLEM DESCRIPTION

9.4.1 Water Concentrations

Four metals of concern were identified in the March 1998 Draft Water Quality Program Plan: mercury, copper, cadmium, and zinc. Mercury is addressed separately from the other metals as it is more well defined and has fewer overlapping potential mitigation measures than the other metals.

Cadmium and zinc are addressed briefly here due to lack of data and lack of evidence that these metals cause environmental harm. Other metals such as chromium and lead have been suggested as potentially significant to Bay-Delta water quality. Data on chromium and lead will be sought and evaluated to further determine their potential significance.

Elevated levels of copper have been found in river water at various times of the year. Copper has serious toxic effects on aquatic life. Investigations have identified three main sources of copper in the Bay-Delta ecosystem: abandoned mines, agriculture, and urban runoff. Other sources may exist that are not well documented.

For six sampling periods between July 1996 and June 1997, the USGS prepared colloid (small “clay” particles in water) concentrates, using a tangential flow ultra-filtration of large (~100 liter) water samples from six main stem Sacramento River sites (below Shasta Dam, below Keswick Dam, at Bend Bridge, at Colusa, at Verona, and at Freeport), plus the Yolo Bypass at Interstate-80 (during high flow). The concentrates were analyzed for total metals, and some also were subjected to sequential extractions to determine forms of metals (speciation).

It generally was found that the sum of dissolved and colloidal concentrations using ultra-filtrates and colloid concentrate samples was a more reliable way to estimate total water-column loadings than conventional whole water analyses.

A significant proportion of the trace-metal loading in the Sacramento River occurs from metals in colloidal form (grain size between about 0.005 and 1.0 micrometer (μm)). Colloids represent the dominant form of aluminum, iron, and lead in the water column, and are an important factor in the distribution of other trace metals. Generally speaking, the colloidal fraction of copper is higher than zinc, and the colloidal fraction of zinc is higher than cadmium.

The influence of metal-laden acidic drainage from the Iron Mountain Mine site (via Spring Creek and the Spring Creek Arm of Keswick Reservoir) is apparent in

Investigations have identified three main sources of copper in the Bay-Delta ecosystem: abandoned mines, agriculture, and urban runoff. Other sources may exist that are not well documented.

water samples from the site below Keswick Dam, where occasionally water quality standards for copper ($5.6\mu\text{g/l}$, based on a hardness of 40 mg/l) have been exceeded). The water quality standard exceedances continued in January 1997, despite ongoing operation of the lime neutralization plant at Iron Mountain, which reportedly removes about 80% of copper loads and about 90% of zinc and cadmium loads from Spring Creek.

In mid-December 1996, conventionally filtered copper concentrations were from 4.6 to $5.1\mu\text{g/l}$, and zinc ranged from 6 to $9\mu\text{g/l}$. During flood conditions in early January 1997, conventionally filtered copper concentrations were from 4 to $9\mu\text{g/l}$, and zinc ranged from 9 to $16\mu\text{g/l}$. Ultra-filtrates ($0.005\text{-}\mu\text{m}$ equivalent pore size) of water samples from below Keswick Dam in December 1996 and January 1997 contained copper concentrations about 40–70% lower than the conventional (0.40- and $0.45\text{-}\mu\text{m}$) filtrates. In 1998, the USGS reported that zinc concentrations were 10–50% lower, indicating significant colloidal transport of copper and, to a lesser extent, of zinc.

The proportion of cadmium, copper, lead, and zinc loads entering the Bay-Delta that are associated with the areas above Keswick Dam can be estimated by comparison of metal loadings at Keswick Dam with those at the site sampled furthest downstream, generally at Freeport (plus the Yolo Bypass, when flowing). The results highly depend on the flow regime, as shown below.

The proportion of cadmium, copper, lead, and zinc loads entering the Bay-Delta that are associated with the areas above Keswick Dam can be estimated by comparison of metal loadings at Keswick Dam with those at the site sampled furthest downstream.

Proportion of Cadmium, Copper, Lead, and Zinc Loads Entering the Bay-Delta by Flow Regime

Date	Flow Regime	Metal (%)			
		Cadmium	Copper	Lead	Zinc
December 1996	Moderately high flows	90	35	10	50
January 1997	Flood conditions	23	11	2	15
May-June 1997	Irrigation drainage season from rice fields	81	50	22	96

Note: The above estimates must be qualified by loadings from Colusa in December 1996 and Verona in May-June 1997. Loadings do not account for other inputs from urban sources.

Available data suggest that trace-metal loadings from agricultural drainage may be significant during certain flow conditions; however, additional scrutiny of these data is needed before definitive conclusions can be drawn. Loadings data for copper in July and September 1996 and May-June 1997 show increases in dissolved and colloidal copper and in colloidal zinc between Colusa and Verona,

the reach of the river along which the Colusa Basin Drain and the Sacramento Slough and other agricultural return flows are tributaries. Monthly sampling of these two agricultural drains by the USGS NAWQA Program shows seasonal variations in metal concentrations. For example, dissolved (0.45- μ m filtrate) copper concentrations in the Colusa Basin Drain reached 6 μ g/l in May 1996 and 3 μ g/l in June 1997, whereas dissolved copper in the Sacramento Slough reached a maximum of 4 μ g/l in December 1996.

To put the copper loadings associated with agricultural drainage in perspective, the total (dissolved plus colloidal) loadings of copper from the Colusa Basin Drain in June 1997 were 39.7 lbs/day, whereas the loadings of copper from Iron Mountain Mine via Spring Creek were 44 lbs/day during the same sampling period. Overall, the majority of copper and zinc loading appears to enter the river upstream of Colusa and therefore upstream of the influence of the most intense agricultural drainage return flows in the Sacramento River Basin.

Fine-grained, metal-rich sediments in the Spring Creek Arm of Keswick Reservoir and in the main channel of Keswick Reservoir between the Spring Creek Arm and Keswick Dam were inventoried by USGS in 1993 at more than 200,000 cubic meters. The sediments have been sampled as part of EPA's Remedial Investigation. Extremely elevated concentrations of cadmium, copper, and zinc have been found in sediments and pore waters from sediments in the Spring Creek Arm of Keswick Reservoir.

Fine-grained, metal-rich sediments in the Spring Creek Arm of Keswick Reservoir and in the main channel of Keswick Reservoir between the Spring Creek Arm and Keswick Dam were inventoried by USGS in 1993 at more than 200,000 cubic meters.

Lead-isotope data in colloid concentrates and bed sediments provide a useful "fingerprint" that can be used as a natural tracer for lead pollution from Iron Mountain Mine drainage via Spring Creek and Keswick Reservoir. In streambed sediment and suspended colloid samples taken during 1996 and 1997, the source of lead pollution from the Iron Mountain Mine is a relatively significant component of the total lead found at sampling sites near Redding and Anderson, a much lesser component at Balls Ferry, and a relatively minor component of the total lead loads at Bend Bridge (near Red Bluff) and at sites further downstream.

DWR measured concentrations of 9 trace metals in May and September at 11 stations in the Bay-Delta and in Suisun Bay from 1975 to 1993. Trace metals frequently exceeded guidelines for marine and fresh-water toxicity and for drinking water standards. Trace metals (most frequently copper) exceeded guidelines for fresh-water acute and chronic toxicity 34 times. Marine acute and chronic toxicity guidelines were exceeded 181 times, 160 of which were for copper. Most exceedances were in the upper estuary. Cadmium and zinc rarely exceeded toxicity or drinking water guidelines, and chromium never did.

The Sacramento Stormwater Management Program has prioritized chemicals for the development of proactive pollutant reduction programs, in accordance with a municipal stormwater permit. Copper is one of the constituents of concern that

has been investigated to identify potential sources, prioritize sources, and identify BMPs. The copper source identification work produced information on the many sources of copper in the urban environment. While some of the sources are not exclusive agents, some contribute significantly on their own. Sources include air emissions, rainfall, tap water, brake pad wear, streets and parking, pesticides, and erosion. Some point source discharges also were considered, such as swimming pool discharge and cooling towers.

Contributions from each source were roughly estimated, using readily available actual measurements where possible and estimations based on results from other studies. The largest single estimated contribution is from automobile brake pad wear. When asbestos was phased out as a brake pad material, the industry began making “semi-metallic” brake pads. These new brake pads incorporated metal alloys into the pad structure, which lead to long-life pads without asbestos. The most common metal used in these semi-metallic brake pads is copper. Using rough estimates of the study, several tons of copper could be discharged in the urban areas in the Bay-Delta region each year from automobile brake pad wear.

The methodology used in the estimations was taken primarily from similar studies conducted in Santa Clara. Noting that urban areas will not differ dramatically in sources of copper, all urban areas throughout the Sacramento and San Joaquin River watersheds will contribute to copper loading in the creeks and rivers from automobile brake pad wear.

Using rough estimates of the study, several tons of copper could be discharged in the urban areas in the Bay-Delta region each year from automobile brake pad wear.

9.4.2 Biological Effects

Until recently, most of the information on toxicity of metals was derived from acute toxicity tests. The toxicity tests in the USGS study address bioaccumulation. Toxicity of particles of metals also has not been well studied. Although not well documented, it is thought that toxicity to fish eggs is caused by higher concentrations of copper particles.

The USGS assessed bioaccumulation in caddisfly larvae at five sites in the Sacramento River between Redding and Tehama, and at one reference site (Cottonwood Creek near Redding). Samples were taken in October 1996. Cadmium concentrations in caddisfly larvae from Sacramento River sites were enriched from 5 to 36 times the concentrations of those from the reference site. Cadmium concentrations of the whole body ranged from 0.7 to 2.2 $\mu\text{g/g}$ dry weight. Of this total, approximately 60% (from 0.4 to 1.3 $\mu\text{g/g}$ dry weight) was associated with the cell cytosol, an intracellular fraction that is indicative of metal bioavailability. Concentrations in the Sacramento River are comparable to other areas severely affected by mining, such as the Clark Fork River downstream of Butte, Montana. Copper and zinc also showed some enrichment in caddisfly

whole bodies and cytosol fractions; enrichment factors relative to the reference site were 1.4-3.0 $\mu\text{g/g}$. The caddisfly data indicate that bioavailable forms of cadmium persist in the Sacramento River downstream of Tehama.

Consumption of contaminated aquatic invertebrates is a biologically significant pathway for exposures of salmonids to metals. Recent studies show that fish held in clean water and fed a metals-contaminated diet had similar whole-body metal concentrations as fish raised in the water where the food was collected. Fish feeding on clean invertebrates while living in water with elevated metals concentrations exhibited no reductions in survival or growth.

Consumption of contaminated aquatic invertebrates is a biologically significant pathway for exposures of salmonids to metals.

Sediment toxicity at the confluence of the Sacramento and San Joaquin Rivers has been observed for a number of years by the San Francisco Estuary RMP. Metals recently have been identified as the principle component of toxicity in pore space water within sediments. Identification of specific toxic metals still must be completed.

9.5 APPROACH TO SOLUTION

A majority of the work relating to reduction of copper in the Bay-Delta rests on the results of studies that still need to be done. The information presented shows local impacts and temporal excursions above ambient water quality standards in the Bay-Delta. More information is needed to determine effects and specific remedial activities. Appropriateness of specific remedial activities should be determined based on all of the effects data. **No remedial activities on abandoned mine sites should be performed without federal environmental "Good Samaritan" protection. Without this protection, acting CALFED agencies may become responsible parties for the abandoned sites.**

9.5.1 Priority Actions

1. CALFED should participate in studies to better define ecological impacts and the spatial and temporal extent of heavy-metal pollution. Ecological impact evaluations would be performed under the CALFED Ecosystem Restoration Program, in coordination with the Water Quality Program.
2. Remedial activities for cleanup of mines should be implemented as deemed appropriate by impacts on habitat and the feasibility of remediation.

3. CALFED should participate with municipalities on the Brake Pad Consortium and other urban stormwater programs to assist in source reduction.
4. CALFED should continue to work with municipalities on evaluation of stormwater pollution control projects that might reduce loading of copper to the Bay-Delta.
5. Any work to reduce copper from agricultural uses should be coordinated with the RWQCB and the DPR.

9.5.2 Information Needed

Studies are needed to determine the spatial and temporal effects of heavy metals and their ecological significance in the Bay-Delta. Emphasis needs to be placed on monitoring the diet of fish species and sediment, in addition to much of the water samples and acute toxicity tests that have been collected.

Monitoring is required to assist in the study of spatial and temporal effects of metals.

Emphasis needs to be placed on monitoring the diet of fish species and sediment, in addition to much of the water samples and acute toxicity tests that have been collected.

9.5.3 Existing Activities

Municipalities are participating in a Brake Pad Consortium to influence brake pad manufacturers to use other, safer materials.

Clean-up activities are ongoing at the Iron Mountain Mine site above Keswick Dam.

Activities by the Mining Remedial Recovery Company on other mines in the upper watershed are moving toward reducing impacts of those mines.

The Sacramento Ambient Monitoring Program has been collecting data on total and dissolved copper, cadmium, and zinc since 1992.

The USGS and DWR have been collecting metals data, as previously mentioned.

